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Perspectives of spray pyrolysis for facile synthesis of catalysts and thin films: An introduction and summary of recent directions

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ABSTRACT

In the modern technological world, applications are rapidly demanding homogeneous, reproducible, scalable processes for films and catalytic surfaces. The uses of spray pyrolytic methods for fabricating these films have received attention since the late 1980s, and today spray pyrolysis finds use in a variety of applications, ranging from biomedical to industrial, microelectronics to ceramics. In this review, basic parameters of spray pyrolysis for catalytic and thin film formation are summarized, while recent developments in spray deposition for environmental remediation, photovoltaics, fuel cell and battery materials, biomedical applications, and microelectronics are also discussed.

1. Introduction

In the modern technological world, applications are rapidly demanding homogeneous, reproducible, scalable processes for films. The uses of spray pyrolytic (SP) methods for fabricating these films have received attention since the late 1980s, though today spray pyrolysis finds use in a variety of applications, ranging from biomedical to industrial, microelectronics to ceramics. A comprehensive review of spray pyrolysis is a difficult task to undertake; we have thus chosen to restrict ourselves to non-plasma methods, focusing on liquid, powder, and flame-spray deposition techniques. There are many other published reviews and we will mention these here that the reader is referred to for further information. We present a comprehensive introduction to spray pyrolytic techniques in liquid and powder form; as well as a summary of current status of industrial and chemical progress in the field of spray pyrolysis in a variety of disciplines, including photocatalysis, ceramics, and electrocatalysis.

2. Spray pyrolysis parameters

2.1. Atomization of liquids

Spray pyrolysis techniques involve the acceleration of a liquid or liquid/solid phase precursor solution from a specially designed atomizing nozzle (atomizer) to carry a droplet of reagents to a surface or interface. There are various parameters based on which the atomizer are classified. We have based the respective methods on different sources of energy atomizers divided to four classes, liquid and gas energy, mechanical, vibrational, and electrical energy [1]. Our focus is mostly on atomizers in gas energy (pneumatic acceleration), including vibrational (ultrasonic) and electrical energy (electrostatic) devices. Thus, spray pyrolysis is usually classified as air blast or pressurized spray pyrolysis [2], ultrasonic spray pyrolysis [3] and electrostatic spray pyrolysis [4].

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In electrostatic spray pyrolysis, different spraying modes are acquired which were classified by Cloupeau and Prunet-Foch [5] as dripping, micro-dripping, spindles, con-jets and simple jets. Each mode has various droplet size distributions that have effects on film properties.

There are some reports on modifying the process of SP to overcome limitations which are encountered with corona spray pyrolysis [6], improved spray pyro-hydrolysis [7] and micro-processor based spray pyrolysis [8]. This is accomplished by using different atomizers, resulting in different droplet velocities and sizes which impact the properties of the deposited film [9].

2.2. Transportation and evaporation of solvent

The transportation of aerosol droplets from the atomizer to the substrate is part of the deposition process during which shrinkage of droplets occurs as a result of solvent evaporation. The perfect situation is for droplets of precursor reaching the target just as its evaporation has been completed [10]. Filipovic [11] identified four forces which affect aerosol formation, including gravitational, electrical, stroke, and thermophoretic forces. Each of these forces varies substantially as the droplet undergoes continuous vaporization during its path toward the substrate.

Computer modeling of the spraying process should include variation in these forces. Chen [12] calculated the flight time of droplets in an ESD process for small distances which allowed for assumptions such as constant electric fields, but ignored assigning a solvent evaporation parameter. Based on interfacial tension between substrates, gases and droplet liquids, spreading of droplets varied. The rate of droplet flattening was reduced as the viscosity of the solution was elevated [12]. Lampkin [13] has studied the aerodynamics of nozzles in which the velocity and direction of atomization are important factors in droplet impact on targets.

Some simulations have been reported on the effect of impact properties (droplet velocity and size) on the fattening ratio in the scale of atoms. Shimizu et al. [14] has evaluated the fattening ratio for Al droplets and drawn the conclusion that the flattening ratio is enhanced by increasing droplet size and velocity.

The evaporation of solvent occurs parallel to droplet transportation, landing, and spreading on the substrate. This effect leads to droplet size reduction and then formation of precipitates. In the electrospray deposition (ESD) process, droplet disruption may be observed during evaporation defined as the splitting of one charged droplet to a few smaller ones when its charge density reaches the maximum amount [12]. Depending on temperature and droplet size, various types of products reach the target surface (wet droplet, dry precipitate, vapor, or powder) [10,15] which will be discussed later.

The flow rate of precursor to the nozzle controls the spray rate and amount of deposited film on the target. The flow rate (f) of the aerosol itself is affected by a proportionality constant K and the square root of liquid characteristics such as viscosity (μ), vapor pressure (P), and surface tension (σ) [16]. The following equation shows this correlation:

$$f = K\sqrt{\frac{P}{\mu\sigma}} \tag{1}$$

Based on the above equation, if any enhancement of the viscosity occurs in the solvent, the flow rate changes accordingly. As any additives in the precursor causes changes in the viscosity and surface tension of solvent, the flow rate varies through the nozzle and must be accounted for when designing spray deposition experiments [16].

Perednis et al. have studied the flow rate parameter in ESD and pressurized spray deposition (PSD) [17]. Their investigation shows that changing the flow rate of precursor has a significant influence on the process. As a result, ESD (with the normal flow rate of 1–8 mL/h) is more sensitive to flow rate parameters than PSD (normal range of flow rate 30–120 mL/h). At lower feed rate of precursor in the ESD process, denser homogeneous thin films can be regularly synthesized. In both processes though, the higher the flow rate, the higher the possibility of film cracking, due to many of the previously noted processes. The related concept of droplet formation and droplet entrainment is illustrated in Fig. 1 showing the formation of deposits from TiO_2 aerosol-derived films [18]. The effects of droplet size, evaporation rate, substrate distance, and flow rates can be illustrated as having major consequences for deposited films.

2.2.1. Particles

The previously discussed pyrolysis techniques describe liquid precursors carrying metallic or polymeric solutes being sprayed. However, the original spray deposition techniques were originally conceived for nano-scale powders in suspension [19]. Preparation of field effect transistors [20], carbon nanotubes [21], and thin films [22] have been carried out by the aerosol method. To produce particles and powders, a typical spray pyrolysis setup as discussed before (and similar to thin film synthesis set ups) includes precursor solutions, aerosol generators or atomizers, reactors or hot furnaces and collectors for product [23].

Aerosols are defined as a suspension of solid or liquid particles in a gas medium. To prepare particles by aerosols, two different methods are applicable which include vapor deposition techniques and spraying of a liquid-phase precursor. Preparing particles by generating aerosols has several advantages: controllable crystallite size, morphology and composition of particles, low cost operation, continuous operation, and high rate production [24]. Recent improvements in the designs of spraying nozzles prevent issues such as clogging and breaking of the nozzle by pressure buildup. Once an aerosol is formed, the spray is directed toward a furnace in which solvent evaporation, component diffusion, forming precipitates, and pyrolysis may occur. A substrate for film formation may be housed in such furnaces.

Size, size distribution and morphology of particles are manipulated by controlling the droplets in the aerosol, and their environment of atomization. Atomization is classified as jet, swirl, jet-swirl, pneumatic, rotary, acoustic, ultrasonic and electrostatic [1] depending on the nozzle geometry and spray technique. There are some review papers on synthesizing particles via spray pyrolysis techniques [19,24,25]. Of note is the review by Jung et al. [25d], which points to enhancement of research work on spray pyrolysis in recent years.

2.3. Spray pyrolysis techniques – flame spray pyrolysis

A search for “flame spray synthesis” on ScienceDirect returns 1899 articles as of September 26th, 2013 since 2010; More than 450 articles came out each year, and has covered topics including fuel cells, thin films, photocatalytic activities, NO_x emissions, diesel fuel, calcium phosphate, heat transfer, ZnO nanoparticles, and carbon nanotubes. Flame spray pyrolysis (FSP) utilizes similar methodology at the previously listed spray techniques; precursors can be liquid/liquid phase, or a suspension of particles in a liquid which is sprayed via an atomizer. In flame-spray pyrolysis, the outlet stream is passed through a methane or hydrogen-fueled flame, resulting in fast combustion, solvent evaporation and pyrolysis, affording nanoparticles of varying morphologies. Temperatures of spraying can reach 2000 K at the outlet; and the resulting spray can be trapped in a collector or subjected to further pyrolysis.

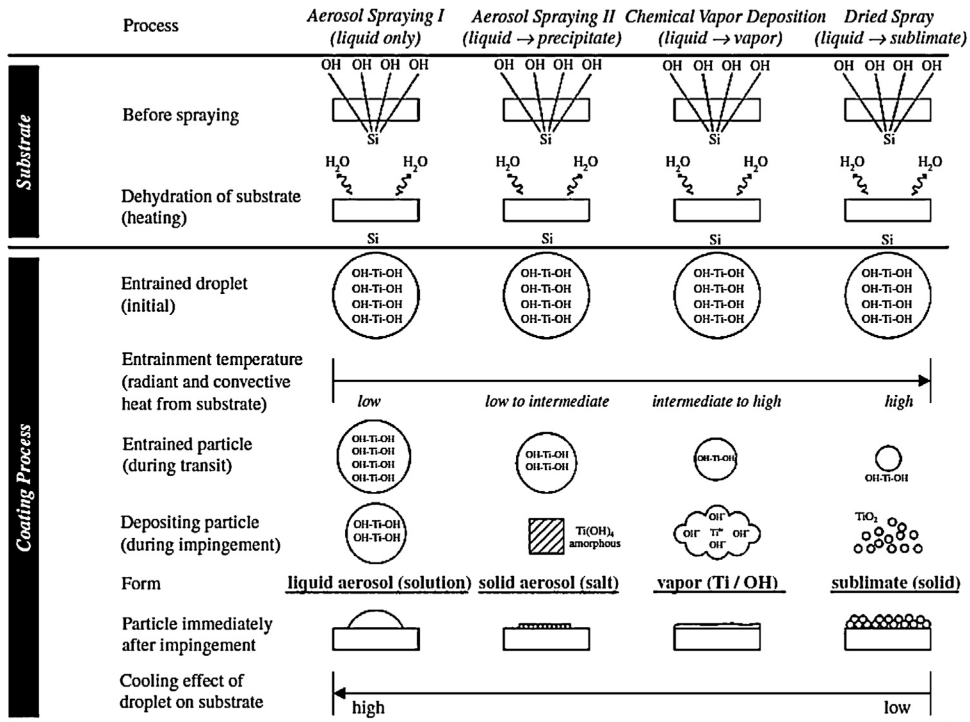


Fig. 1. Formation of TiO_2 from Ref. [18] showing droplet entrainment for several aerosol vapour techniques. Used with permission from Ref. [18].

The authors acknowledge a recent review by Strobel [26] which approaches the topic clearly.

2.4. Spray pyrolysis is comparison with other thin film and particle synthesis techniques

The previously discussed controllable factors influencing spray pyrolysis techniques make the practice applicable in many areas, but to make the process desirable the technique must exhibit benefits over competing techniques. For synthesis of powders from liquid precursors, spray pyrolysis offers small particle size distribution [27], precise precursor dosing control, and ambient pressure processing. Compared to tradition al synthesis techniques (reflux, solid state, pyrolysis) spray pyrolysis can be used in many of the same process conditions; though through modifying process conditions one may exercise precise control over relevant synthesis parameters (doping levels, particle size, atomization technique, calcination temperature).

The benefits of the spray pyrolysis system is clear in Table 1 which compares different deposition methods including chemical vapor deposition (CVD), atomic layer deposition (ALD), sol gel spin coating, sol gel drain coating and spray pyrolysis (SP) techniques for two common metal oxide systems (Co_3O_4 and ZnO). For both products, spray pyrolysis offers spherical nano sized grains at moderate temperature under room atmosphere, without the need to deposit film under pressure or vacuum.

When fabricating thin films, spray pyrolysis offers benefits versus comparable techniques, such as dip/spin coating, drop coating and chemical vapor deposition. Films can be deposited on nearly any substrate, similar to many other film techniques. By moving the nozzle, (i.e. a hand-held sprayer) coatings may be applied in ambient conditions over wide areas on non-planar surfaces [39], a restriction on dip/spin coating. Versus vapor deposition, spray deposition allows films to be deposited over a substrate in non-vacuum conditions using easily-handled liquid or liquid/solid slurry precursors. As with most film techniques, substrate preparation is key to the film's adhesion qualities, while film morphology

Table 1
Synopsis of current synthesis techniques for cobalt and zinc oxides.

Film composition	Method of deposition	Morphology	Condition (temp/pressure)	Ref.
Co_3O_4	CVD	Round grain	350–500 °C/2–10 mbar	[28]
	CVD	Trigonal pyramidal shape	360–540 °C/10 Torr	[29]
	Laser CVD	Leaf-like	10^3 mbar	[30]
	ALD	Preferential orientation	100–400 °C/10^{-5} mbar	[31]
	SP	Spherical nano-sized grains	350 °C/no pressure	[32]
	Sol–gel spin coating	Spherical-elongated grain	400–700 °C	[33]
ZnO	CVD	Elongated grains	360 °C	[34]
	ALD	Spherical and worm-like grains	400–1000 °C/40–65 Pa	[35]
	SP	Spherical nano-sized grains	430–610 °C/no pressure	[36]
	Sol–gel drain coating	Spherical grains	350 °C	[37]
	Deep coating	Spherical grains	200–500 °C	[38]

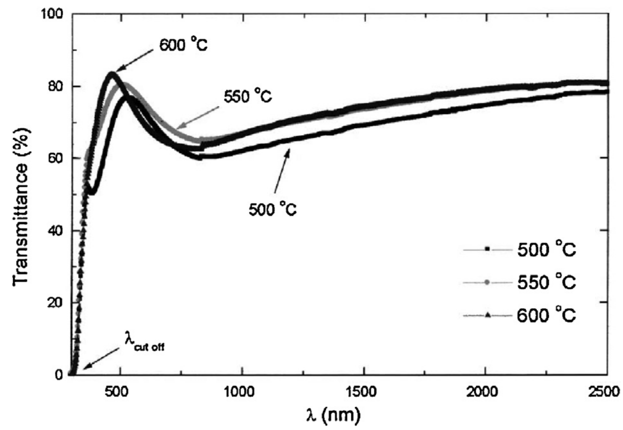


Fig. 2. Transmission spectra of TiO_2 layer on glass substrate.
Reprinted with permission from Ref. [47].

can be influenced by process parameters as well as chemical composition [40].

3. Applications of spray pyrolysis

3.1. Photocatalysis: titania dioxide and zinc oxide thin films for environmental remediation

Heterogeneous photocatalysis is one of the important and growing topics in environmentally friendly catalyst research. Extensive research had already been performed and is underway for the elimination of hazardous waste from the environment [41,42] After the discovery of photocatalytic splitting of water on titanium dioxide (TiO_2) electrodes by Fujishima and Hunda [43], small semiconductor materials have attracted several interests for environmentally friendly photocatalysis [42,44]. Much work was also performed focused on hydrogen production from water photocatalytically [45], which can serve as an alternate solar energy source. To understand the effects on the catalyst structure investigation, the preparative method is very important. Among many other preparatory processes, Spray Deposition is one of the interesting and attractive methods for the preparation of semiconductor nanocrystals. Low cost manufacturing, simple manipulation, and applicable large scale synthesis present spray pyrolysis techniques of profound interest [46].

Many examples of chemical spray pyrolysis techniques have been used to prepare semiconductor nanocrystals with photoelectronic properties. Helal et al. designed a novel spray pyrolysis method to fabricate nanometer thick TiO_2 films on glass substrates [47]. The increase of deposition temperature (500–600 °C) results improve of transmission of TiO_2 films due to the increase of film crystallinity (Fig. 2) Photocatalytic transformation of traces of methanol conversion to formaldehyde in water was observed. The photocatalytic activity increases with the increase of deposition temperature and time due to formation of more condensed materials and increase of porosity.

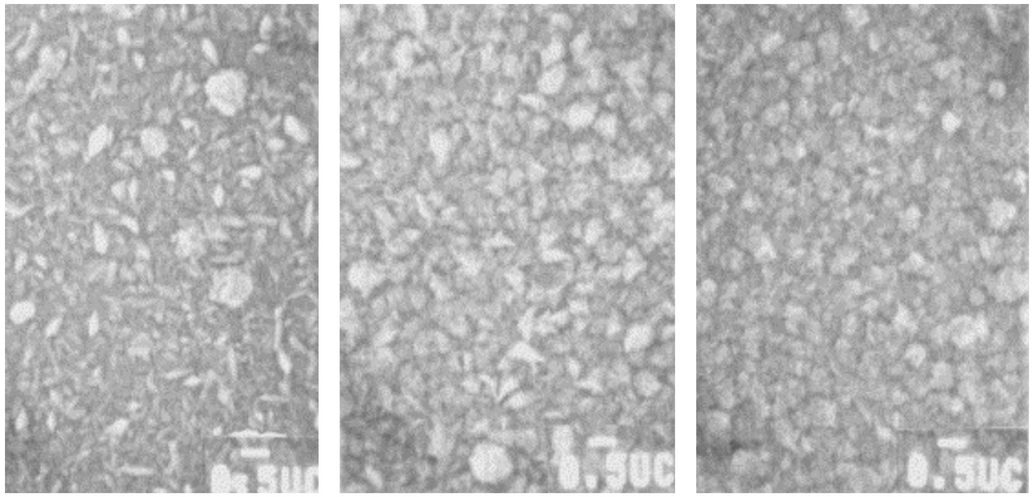
Research is underway [48] to degrade dye pollutants, discharged from petrochemical, textile, and other industries. It has been demonstrated that porous immobilized materials can serve as good photocatalysts for dye degradation, which can be separated easily after use. FSP techniques were used to synthesized TiO_2 and ZnO films [49]. Different phases of TiO_2 (rutile, anatase and mix phase) were obtained depending on the substrate temperature and deposition time. Excellent photocatalytic degradation of dyes were obtained using these catalysts, with the aid of UV radiation (used to excite the wide band gap in TiO_2) [50] This has the consequence of resulting in poor energy efficiency. Therefore, it was necessary to modify the TiO_2 to extend the spectral response in the visible region [40a].

Tian et al. doped vanadium in TiO_2 using simple one-step FSP, which enhances the catalytic activity for the degradation of methylene blue and 2,4-dichlorophenol under visible light as compared to the undoped TiO_2 [51]. Apart from incorporation of transition metal ions, Nitrogen and Fluorine ions have also been doped inside the TiO_2 structure to achieve visible-light driven photocatalysis [52,53]. Spray pyrolysis techniques were used to co-dope N and F atoms in TiO_2 crystals with a porous and acidic surface; as a consequence highly reactive visible light driven photocatalysis was achieved. The concentration of dopants can be controlled by adjusting the temperature of spray pyrolysis. Additionally to TiO_2, zinc oxide (ZnO), which serves as an alternate to TiO_2, due to a closer energy band gap value to TiO_2, can also synthesized. Highly porous ZnO films were prepared by Quintana et al. by spray pyrolysis methods (Fig. 3) [54] and its photocatalytic activity was investigated by degradation of methyl orange with the intermediate reaction product hydrazine. The photocatalytic performance increased with films having high surface area, deposited at high pH.

Doping can be induced in ZnO by spray pyrolysis to improve the photocatalytic activity. The dopant concentration and surface morphology can be controlled by varying the substrate temperature and solution flow rate of spray pyrolysis. Nitrogen-containing ZnO was synthesized using spray pyrolysis, which showed superior photocatalytic activity in decomposition of acetaldehyde than pure ZnO under visible light radiation [55]. One step flame spray pyrolysis was used to synthesize Au-ZnO and Pt-ZnO nanocomposites with average crystalline sizes between 3 and 5 nm [56]. The Au-ZnO exhibited superior photocatalytic performances than undoped ZnO and TiO_2 in methylene blue degradation. Retardation of recombination of photo induced electron–hole pairs by shifts in the Fermi level of Au-ZnO is the reason behind the enhanced photocatalytic activity. Al doped ZnO with tunable particle sizes and surfaces were synthesized by spray pyrolysis [57]. The Al-doped ZnO performed better than the nondoped ZnO in degradation of methylene blue.

3.2. Photocatalysis: hydrolysis via photo and electrochemical means

Another photocatalytic reaction in which SP techniques have been applied involves hydrolysis for productions of H_2 and O_2 from water, which can serve as a clean and renewable energy source [58]. Two important material properties related to the photocatalyst includes the surface area and crystallinity of the material. The ability to tune these properties was demonstrated by changing the operation conditions like temperature, precursor concentration, and proper selection of organic solvent. Flame spray pyrolysis was used to synthesize a series of titania and gold modified titania, where the choice of xylene solvent made the titania material more active than other materials in photocatalytic production of H_2 by water photo-splitting and methanol reforming [59]. Li et al. deposited thin films of zinc-indium sulfide ($ZnIn_2S_4$) on ITO coated glass substrates for applications in electrolysis of water electrochemically or through photo-electrochemical methods [59]. A one step, continuous, template free production of nanostructured bismuth vanadate ($BiVO_4$) was produced using ultrasonic spray pyrolysis, which shows significantly superior photocatalytic activity compared to commercial $BiVO_4$ in photocatalytic O_2 production from $AgNO_3$ solution [60]. The particles range from thin hollow and porous shells to solid spherical moieties. Differences in particle morphology by the decomposition of the gases inside the shell by SP methods are the reasons for the enhancement.



(a) (b) (c)

Fig. 3. SEM image of ZnO from Ref. [39] on SnO substrate under different annealing temperatures. Used with permission from Ref. [54].

3.3. Photovoltaics and dye sensitized solar cells

In the field of alternative and clean energy, the dye sensitized solar cell (DSSC) is an active area because of its low cost and simple manufacturing [61]. Spray pyrolysis deposition (SPD) is a promising preparation process to prepare large scale films for this application. Okuya et al. fabricated TiO_2 films as working electrodes for DSSC's by combination of SPD and conventional electrode production processes [62]. The conversion efficiency was as high as 3.2% due to modification of TiO_2 surfaces by optimizing the aluminum dopant in the synthesis. The SPD method was utilized by T. Kawashima et al. to produce a new transparent conductive film (FTO/ITO film), where F-doped tin oxide (FTO) was deposited on indium-tin oxide (ITO) [63]. The films remained conductive even at high temperature (up to 600 °C) and gave high energy conversion efficiency (3.7%).

3.4. Ceramics

Various spray pyrolysis techniques have been used for production of ceramic powders directly from solutions. Physical and chemical flexibilities of the SP processes lead to synthesis of ceramic materials having a wide range of size, composition, and morphology. Controlled atomization, coagulation, evaporation, thermolysis, and sintering processes are required to obtain controlled characteristics in ceramic powders [19]. Precursors, atomization, evaporation period, droplet coagulation, thermolysis, and sintering during spray pyrolysis are key factors for ceramic powder production.

Acharya [64] described the use of spray coating method for the synthesis of nanoporous carbon membrane that had remarkable size selectivity of oxygen over nitrogen. The synthetic method incorporated a solution of 50:50 polyfurfuryl alcohol in acetone as the carbon precursor, which was sprayed onto stainless steel disk supports. Reproducibility and simplicity – these two important aspects of the spray coating method were proved to be useful for the desired synthesis.

Combustion spray pyrolysis is another method for preparation of new materials used in ceramic thermal barrier coatings (TBC). Yttria stabilized zirconia (YSZ) and yttrium aluminum garnet (YAG) have been considered as the best TBC materials for their high thermal stability and low thermal conductivity. Saravan et al. described the use of combustion spray pyrolysis (or flame SP) for the synthesis of $Y_3Al_5O_{12}$ and ZrO_2–8 mol% Y_2O_3 films [65]. An aqueous solution of nitrate salts of aluminum, zirconium and yttrium was used to synthesize thin films of Al_2O_3–37.5 mol% Y_2O_3 ($Y_3Al_5O_{12}$, which crystallizes as yttrium aluminum garnet) and ZrO_2–8 mol% Y_2O_3. They were successfully deposited on many substrates including deposition by chemical and ultrasonic methods on cleaned amorphous silica, stainless steel, and FeCrAlY bond coat.

3.5. Fuel cell materials and batteries

Flame spray pyrolysis has been demonstrated in applications such as electrodes and electrolyte fabrication [66] for fuel cells [67]. Nano-sized crystalline perovskites $La_{0.6}Sr_{0.4}$ $Co_{0.2}Fe_{0.8}O_{3-d}$ was prepared as cathode material for intermediate-temperature SOFCs (about 600 °C) at notably high rates (400 g h^{-1}), without sacrificing surface area. The material shows a pronounced increase of conductivity at favored lower temperatures, mainly attributed to its mixed nature at the atomic scale [67]. Realizing appreciable advantages, these applications still suffer the adverse effects due to the gap of thermal expansion coefficients between the cathodes and electrolytes, which remains a challenge.

In situ spray pyrolysis techniques can be used as inexpensive, cost effective, and commercially viable methods for the synthesis of battery materials like carbon coated Si-nanocomposites [68]. Carbon coated Si nanocomposites are used as highly efficient anode materials for Li-ion batteries. In this work the researchers prepared a mixture of nano sized Si-particles (<100 nm) with citric acid/ethanol solutions by ultrasonication. The mixture was then spray pyrolyzed in air using a flow rate of 4 mL/min. at different processing temperatures (300–500 °C) resulting in carbon coated spheroidal Si-nano particles.

Silica encapsulated ferromagnetic cobalt oxide (CoO) nanoparticles were synthesized by ultrasonic spray pyrolysis methods [69]. An aqueous mixture of silica colloid, styrene, ethylene glycol dimethacrylate, AIBN, 1,4-dioxane and 0.01 M SDS was nebulized by using an ultrasonic humidifier and inert gas (N_2 or Ar, flow rate, 1 SLPM) and two furnaces at 200 °C and 700 °C (Fig. 4). The black magnetic colloidal particles were isolated by centrifugation.

Nano-scale sized FSP made metal oxides, e.g. V_2O_5 (30–60 nm) offered exceptional specific charge capacities at higher discharge rates, comparing to microparticle counterparts. By optimizing the spray flow rate and electrochemical cycling window of the active

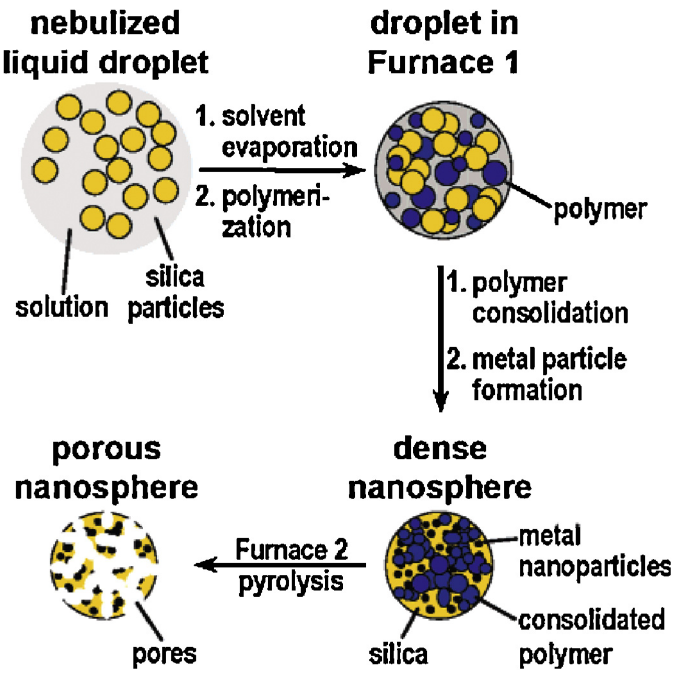


Fig. 4. Formation of porous cobalt nanoparticles encapsulated in an oxidation-preventing polymer.
Used with permission from Ref. [69].

materials, the spray-synthesized oxides exhibited much higher rate capabilities than microstructured vanadium oxide, which the authors attribute to shorter Li^+ diffusion path length as a result of flame spray synthesis [70]. Iron phosphate on carbon ($FePO_4$/C) was also developed as cathode materials for lithium ion batteries showing promising charge capacities [71], due to its nano size (70 nm) produced by FSP. This method also features a two-step synthesis by combining $FePO_4$ made by a first FSP step followed by another solid state synthesis of incorporating a lithium and a carbon source. Therefore, versatile applications of FSP are integral or parts of synthetic design.

3.6. Biomedical applications: supplements

Flame-spray pyrolysis synthetic strategies can be utilized for synthesizing supplements and supports for enhanced biocompatibility. Iron phosphates containing mainly amorphous nanoparticles [72] (10–20 nm) are suitable for achieving good solubility in dilute acid, and more importantly can be done at large scales. FSP-synthesized Fe_2O_3 coated in situ with silica was produced via addition of hexamethyldisiloxane in the nitrogen carrier stream. Suitable for medical applications, the magnetization is retained while coated in silica films [73]. Recently, silica coated Y_2O_3:Tb^{3+} nanoparticles were made by FSP and can be used as nanophosphors in bioimaging applications [74]. Nevertheless, based on the wide application of FSP synthesized nanomaterials, health and handling effects were also investigated [75], revealing that FSP-silica coatings are safe when used in industrial production.

4. Recent directions

As a major successful application of flame spray pyrolysis in manufacturing TiO_2 commercially at a large scale [76], this technique has been exploited extensively in synthesizing metal oxides, mixed metal oxides, perovskites, metals and metal salts. With unique properties shown in contrast to conventional sol–gel process [77], the list of applications of these newly created materials continues to grow [26a,b].

Recent work on FSS covers most previously mentioned applications and has expanded the synthesis of new materials and their applications in numerous fields. A ceria-supported copper system reported by Kydd et al. is active in CO preferential oxidation due to the ideal dispersion of active components by using FSP. This represents advanced control of the active sites realized in mixed metal oxides systems [78]. A modified synthesis forms $Cu/Ce_xZr_{1-x}O_2$, which affords good activity in NO reduction by CO under low temperature (<350 °C) [79]. MoO_3/SiO_2–Al_2O_3 were also made by FSS in catalyzing the metathesis of light olefins. This material shows enhanced activity accounting for the highly dispersed monometic molybdate over the surface of the support, a quality afforded exclusively by FSS methods over other synthetic strategies [80]. The obvious advantage of these materials lies in their highly efficient synthesis as compared with other methods such as hydrothermal [81] and reflux [82] techniques for synthesizing active components/support materials. The wide range of noble metal supported material made by FSS finds applications in hydrogenation, NO_x reduction, oxidation catalysts, and sensors [26c].

For example, noble metals supported on SiO_2–Al_2O_3 were prepared by FSP; tuning of the acidity was simply facilitated by regulating the amount of SiO_2, which contributed to the boosted catalytic activity in hydrogenation reactions [83]. The gas sensing applications of these noble metal supported metal oxides expanded quickly, which covers the detection of acetylene, hydrogen, nitrogen oxide, carbon dioxide, hydrogen sulfide and other environmentally hazardous gases [84]. FSP plays an essential role as a facile single-step synthesis in combining semiconducting metal oxides (e.g. WO_3, ZnO, In_2O_3, SnO_2 and TiO_2) with many dopants [84b].

4.1. Double flame spray pyrolysis

In terms of recent progress on reaction processes, a two-nozzle flame synthesis largely improves the NO_x storage activity, attributed to the Al_2O_3 and $BaCO_3$ nano particles produced independently plus more control of the flaming system [85]. This double-flame system recently showed activity in Fischer–Tropsch reactions on an FSP made Co/Al_2O_3 unmatched with its counterpart made by a single flame pyrolysis [86]. The double flame offered merits like flexibility, adjustable composition and particle size by simply controlling the distance of two flames, and as such, research on this technique could lead to a new era of FSP [85,86].

5. Conclusions

It is shown that spray pyrolytic methods are versatile and applicable synthetic techniques for creating novel and impressive materials. With a wide range of applications in technology and industry, spray methods afford an experimenter synthetic control which allows for the creation of novel catalysis, films, active materials and supports. The process is easily scalable, repeatable, and allows many avenues for continued investigation from both academic and industrial interests.

Acknowledgements

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